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# Sources, cycling and export of nitrogen on the Greenland Ice Sheet

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## Abstract

Fjord and continental shelf environments in the Polar Regions are host to some of the planet's most productive ecosystems, and support economically important fisheries. Their productivity, however, is often critically dependent upon nutrient supply from up-stream terrestrial environments delivered via river systems. One of the most extensive glacially-fed coastal ecosystems is that bordering the Greenland Ice Sheet. The future primary productivity of this marine ecosystem, however, is uncertain. A potential increase in primary productivity driven by reduced sea ice extent and associated increased light levels may be curtailed by insufficient nutrient supply, and specifically nitrogen. Research on small valley glaciers indicates that glaciers are important sources of nitrogen to downstream environments. However, no data exists from ice sheet systems such as Greenland. Time series of nitrogen concentrations in runoff are documented from a large Greenland glacier, demonstrating seasonally elevated fluxes to the ocean. Fluxes are highest in mid-summer, when nitrogen limitation is commonly reported in coastal waters. It is estimated that approximately half of the glacially-exported nitrogen is sourced from microbial activity within glacial sediments at the surface and bed of the ice sheet, doubling nitrogen fluxes in runoff. Summer dissolved inorganic nitrogen fluxes from the Greenland Ice Sheet (30–40 Gg) are a similar order of magnitude to those from a large Arctic river (40 Gg, Holmes et al., 2012). Nitrogen yields from the ice sheet (100–160 kg TDN km<sup>-2</sup> a<sup>-1</sup>), however, are approximately double those from Arctic riverine catchments. We assert that this ice sheet nitrogen subsidy to Arctic coastal ecosystems may be important for understanding coastal biodiversity, productivity and fisheries, and should be considered in future biogeochemical modelling studies of coastal marine productivity in the Arctic regions.

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# 1 Introduction

The availability of nitrogen widely limits primary productivity in fjord (Rysgaard et al., 1999), coastal (Poulsen and Reuss, 2002; Daly et al., 1999; Nielsen and Hansen, 1999) and open ocean (Smith et al., 1985; Moore et al., 2002) waters bordering the Greenland Ice Sheet (GrIS) in summer. These Greenlandic waters are some of the most productive ecosystems in the world, and boast high socio-economic value via fisheries (e.g. shrimp, halibut) (Hamilton et al., 2000). In the North Atlantic, primary productivity also draws down CO<sub>2</sub> from the atmosphere and has an important regulatory effect on global climate (Sabine et al., 2004). Warmer ocean temperatures and a lengthened growing season in the Arctic are predicted in future decades. However, increases in marine primary productivity may be capped by intensified summer nitrogen limitation (Vancoppenolle et al., 2013). The GrIS discharges > 1000 km<sup>3</sup> of freshwater annually to the Arctic Ocean, Irminger Sea, Labrador and Greenland Seas (Bamber et al., 2012) but has yet to be evaluated as a source of nitrogen to these waters. This freshwater flux is increasing (Bamber et al., 2012), and will continue to do so as rising air and ocean temperatures enhance rates of ice sheet melting and iceberg calving (IPCC, 2007). Greenland ice core data show the ubiquitous presence of low concentrations of dissolved inorganic nitrogen (DIN) in ice and snow, sourced from the atmosphere (Wolff, 2013). Based upon findings from small glacier systems (Hodson et al., 2008; Telling et al., 2011; Boyd et al., 2011), it is plausible that this atmospheric DIN is supplemented by nitrogen cycled into bioavailable forms by glacial biota (Telling et al., 2012; Boyd et al., 2011). While there is a mounting body of literature on nitrogen cycling on valley glaciers (Telling et al., 2011; Hodson et al., 2008), there is comparatively little data on nitrogen sources and cycling on the Greenland Ice Sheet, which is likely to be important as a nutrient source to downstream fjord and marine ecosystems. High reported rates of fjord primary productivity around the GrIS margin (Jensen et al., 1999) and coastal blooms as late as July/August (Frajka-Williams and Rhines, 2010; Nielsen

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and Hansen, 1999) coincident with peak meltwater fluxes (Bartholomew et al., 2011) suggest that such an evaluation will be a fruitful exercise.

This paper documents seasonal time series of nitrogen concentrations, speciation and fluxes associated with runoff at the large (600 km<sup>2</sup>) land-terminating Leverett Glacier (LG) in SW Greenland during the 2012 melt season. A range of contextual field and experimental samples were also collected from sediment laden ecosystems on and beneath the ice sheet (basal ice and incubated basal ice, glacier surface ice, snow, moulin and cryoconite waters) in order to infer the sources of nitrogen species in runoff. Total Dissolved Nitrogen (TDN), DIN (nitrate and ammonium) and dissolved organic nitrogen (DON) were quantified in all samples and ammonium associated with suspended sediments (SS-NH<sub>4</sub><sup>+</sup>) was analysed in runoff. These data were subsequently used to calculate seasonal nitrogen fluxes and yields from the catchment and the Greenland Ice Sheet

## 2 Materials and methods

### 2.1 Field site

Leverett Glacier is located on the south-west of the GrIS, approximately 300 km north of Nuuk (Fig. 1.; 67.06° N, 50.10° W). The glacier overlies predominantly Precambrian gneiss/granitic bedrock, typical of large areas of Greenland (Kalsbeek, 1982). The sub-glacial sediments are primarily Quaternary deposits (e.g. paleosols) containing fresh organic matter that were buried during glacial advance in the last few thousands of years following the Holocene Thermal Maximum when the GrIS margin was positioned tens of kilometres further inland (Simpson et al., 2009). LG supplies runoff to the Watson River during the summer months, the largest of three glacially-fed rivers which supply Søndre Strømfjord (Fig. 1). Søndre Strømfjord is the largest fjord system in western Greenland and comprises an inner fjord (up to 275 m deep, 4 km wide and 80 km long) and a shallow outer fjord (< 100 m deep, 1 km wide and 100 km long) (Nielsen et al.,

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2010). The inner fjord physical oceanography is influenced by meltwater, as indicated by a 50–75 m freshwater surface layer (Nielsen et al., 2010).

2.2 Sample collection, processing and storage

Two main sampling sites were established in summer 2012: one at the ice sheet margin (11 May–15 July) 1 km downstream of the glacier terminus (glacial runoff sampling site, Fig. 1) and one on the ice sheet surface (8 May–9 August) at a moulin located approximately 41 km from the ice margin (surface meltwater sampling site, Fig. 1).

2.2.1 Ice sheet surface sampling

A field camp was established in 2012 in the mid ablation zone at LG at 1030 m elevation, 35 km from the western margin (66.97° N, 049.27° W). Here, samples of meltwater descending to the ice sheet bed via a large moulin were collected from the streams feeding the moulin between 5 May and 9 August (Day 129 and 222). The discharge of meltwater down this moulin was also measured (Supplement Sect. S1). A range of contextual samples were collected, including ice containing dispersed cryoconite debris (“summer ice”) and cryoconite hole waters. Cryoconite holes are water-filled cylindrical melt holes, formed by radiation heating of surface sediment and subsequent melting (Podgorny and Grenfell, 1996). The debris in the base of these holes is termed “cryoconite” which may become distributed over the glacier surface during melt out of cryoconite holes in summer. Ice samples were melted in clean/sterile Whirl-pak™ bags (Nasco) overnight in a warm water bath immediately after collections (melting typically took 2–3 h). All meltwater samples were filtered through 47 mm, 0.45 µm cellulose nitrate filters (Whatman™) in a plastic filter unit (Nalgene™ PES), pre-rinsed 3 times with sample, and stored in high density polyethylene plastic bottles (30 mL). These bottles were frozen immediately after filtration and only thawed out immediately prior to analysis in Bristol. Procedural blanks were processed (n = 5) during the course of the

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sampling season, where deionised water (stored in clean plastic bottles) was treated as a sample and filtered and bottled accordingly.

### 2.2.2 Bulk meltwater sampling

The river draining from the subglacial portal at LG was continuously monitored throughout the 2012 melt season (May–October) using stage measurements in a stable bedrock section ~ 2.2 km downstream of the terminus (Hawkings et al., 2014). Stage was logged every 5–10 min, and converted to discharge using rhodamine dye-dilution experiments (> 30 dye tracing experiments were carried out over the season). Suspended sediment concentrations were calculated as in previous work (Cowton et al., 2012). A turbidity sensor was employed throughout the monitoring period in a similar location to stage measurements. The turbidity sensor was calibrated using manual sediment weight samples. Briefly, a recorded amount of meltwater (usually 300 mL) was filtered through a 0.45 µm cellulose nitrate filter (Whatman<sup>TM</sup>), oven dried overnight at 40 °C and weighed.

Bulk meltwater samples were taken approximately 1 km downstream from the LG subglacial portal, at least once a day during the main melt period (May–July). Samples were collected daily at ~ 10:00 h, with occasional afternoon samples taken at ~ 18:00 h, mostly during subglacial outburst events. A 2 L meltwater grab sample was taken in a HDPE Nalgene<sup>TM</sup> bottle (Thermo Scientific<sup>TM</sup>), which had been pre-rinsed 3 times in the meltwater stream. Samples were filtered soon after collection using a Nalgene<sup>TM</sup> reusable PES filtration stack, and a 47 mm 0.45 µm cellulose nitrate filter membrane (Whatman<sup>TM</sup>). Filtered samples were stored in 28 mL HDPE bottles. Procedural blanks were processed ( $n = 10$ ) during the course of the sampling season, where deionised water (stored in clean Nalgene<sup>TM</sup> HDPE plastic bottles) was treated as a sample and filtered and bottled accordingly. All samples were immediately frozen and stored in the dark until analysis in Bristol.

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### 2.2.3 Basal ice sampling and incubation experiments

Basal ice from the Leverett/Russell Glacier catchment was collected from the ice margin (within 5 km of the main LG bulk meltwater sampling site) by chain saw (30 m × 30 m × 30 m blocks) in spring 2008 and summer 2010. The outermost ~ 0.5 m of ice was first removed before the blocks were cut. The blocks were wrapped in pre-combusted foil and stored at  $\leq -20^{\circ}\text{C}$  prior to processing. Sub-samples of the ice were prepared for nitrogen analysis by chipping ~ 15 cm<sup>2</sup> chunks from the main block using a flame sterilised chisel. The outer ~ 10–30 mm was removed by rinsing with ultra-pure ( $\geq 18.2\text{ M}\Omega\text{ cm}$ ) deionized water, and the remaining ice was transferred into a pre-combusted glass beaker covered with foil. The ice was allowed to melt inside a laminar flow cabinet (Telstar Mini-H) at room temperature. Ice melt was filtered through Whatman polypropylene Puradisc™ 0.45  $\mu\text{m}$  syringe filters. Samples for nitrogen species determinations were stored in clean, thrice-rinsed Nalgene™ HDPE bottles. All sediment and filtered samples were stored in the dark at  $\leq -20^{\circ}\text{C}$  until analytical processing.

Long-term incubation experiments (1–2 yr) were conducted using sediment and meltwater derived from melted basal ice samples, in order to investigate microbially derived sources of dissolved nitrogen in a simulated subglacial environment. Three types of experiments were conducted: (1) live control experiment with no sediment added, where the solution was meltwater from basal ice, (2) live anaerobic experiments (sediment + meltwater from basal ice); and (3) live aerobic experiments (sediment + meltwater from basal ice). The control sediment-free experimental nitrogen concentrations were subtracted from the live (sediment + water) experiments in order to correct for any level of nitrogen species added from the sampling vessel and the original basal ice meltwater matrix. Hence, nitrogen concentrations reported are those that have evolved during the experiment via rock:water contact and in situ microbial activity.

Experiments were performed in the dark at  $0.1^{\circ}\text{C}$  in modified gas-tight 500 mL borosilicate glass bottles. A sampling port towards the base of the vessel immediately

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above the sediment surface was used for meltwater extractions. All incubations contained 100 mL of wet-weight sediment, 200 mL melt water and 200 mL gas headspace. Control incubation experiments contained 200 mL ice melt only. Sediment and ice melt (flushed with O<sub>2</sub>-free-N<sub>2</sub> gas) required for the anaerobic incubations were melted inside a glove-bag filled with O<sub>2</sub>-free-N<sub>2</sub> gas (BOC Ltd, UK). Meltwater/sediments were later flushed with O<sub>2</sub>-free-N<sub>2</sub> gas for > 20 min to ensure that the sediment and water were equilibrated with an oxygen-free atmosphere. The incubations were sampled ~ 2 h after set-up ( $T = 0$  d), on day 4, 109, 190, 294, 382 and 533 and 758 (aerobic only). At each sampling point, 30 mL (15 % of the initial volume) of melt water was removed, filtered through Whatman polypropylene Puradisc™ 0.45 µm syringe filters and stored at ≤ -20 °C until analysis. Sampling of the anaerobic incubation experiments were conducted inside a glove-bag filled with O<sub>2</sub>-free-N<sub>2</sub> gas. All meltwater samples were frozen immediately after collection and stored frozen prior to analysis for dissolved nitrogen species.

## 2.3 Analytical methods

All meltwater samples were analysed for concentrations of total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN, comprising nitrate and ammonium), with dissolved organic nitrogen (DON) determined by difference between TDN and DIN. Concentrations of nitrite were generally below the limit of detection and are not reported. We also analysed ammonium concentrations associated with suspended sediments in runoff (SS-NH<sub>4</sub><sup>+</sup>), where this component is assumed to be bioavailable. The nitrogen content of snow and pre-melt surface glacier ice is taken from previous work conducted in the same catchment (Telling et al., 2012) and from Greenland ice cores (Wolff, 2013). Pre-melt surface glacier ice nitrogen concentrations were taken from previous work conducted in Leverett catchment (Telling et al., 2012). The detailed sampling and analytical procedures are provided in the following sections.

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### 2.3.1 Nitrate

Nitrate was determined using a Thermo Scientific™ Dionex™ ICS-5000 ion chromatograph fitted with an IonPac™ AS11-HC-4 µm anion-exchange column. A 30 mM KOH eluent concentration was used, with an injection volume of 0.4 µL and cell temperature of 35 °C. The detection limit of the instrument was 0.08 µM N. The precision of analyses, determined via analysis of eleven replicate standards within the sample range, was 8.1 %. The accuracy of the machine was determined as -6.4 %, using gravimetrically weighed standards from a 1000 mg L<sup>-1</sup> certified stock standard (Sigma TraceCERT®). All field nitrate data were blank corrected using field procedural blanks. The nitrate concentrations within these blanks were < 0.45 µM for surface samples and below the detection limit for runoff samples.

### 2.3.2 Ammonium

Ammonium was determined manually using the salicylate spectrophotometric method (Bower and Holm-Hansen, 1980; Le and Boyd, 2012), adapted for a smaller sample size (1 mL). The detection limit of the method was 0.6 µM N. The precision of analyses was 4.9 %, calculated from five replicate standards with concentrations within the sample range. Accuracy was calculated to be +0.3 % (from a gravimetrically diluted certified reference standard, Sigma-Aldrich TraceCERT® 1000 mg L<sup>-1</sup>). Ammonium concentrations in field samples were blank corrected using field procedural blanks, and were all above the limit of detection. Mean blank correction factors for ammonium were 0.75 µM N for surface samples. Runoff blank corrections were below the detection limit of the instrument.

### 2.3.3 Total Dissolved Nitrogen (TDN)

Total Nitrogen was determined on most runoff samples, excluding the transect samples, using a Lachat QuikChem® 8500 Flow Injection Analyser system, with digestion unit

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(method number 10-107-04-3-E). The detection limit of the instrument was 1.4  $\mu\text{M}$  TDN, the precision of analyses was calculated as 11.3 % from six 3.6  $\mu\text{M}$  replicate reference standards (gravimetrically diluted from a certified reference standard, Sigma-Aldrich TraceCERT® 1000 mg L<sup>-1</sup>). Accuracy was determined using the same reference standards as -0.4 %. All TDN data were field blank corrected (2  $\mu\text{M}$  for surface samples, and no correction for runoff samples since these were below the detection limit of the instrument).

### 2.3.4 Exchangeable $\text{NH}_4^+$ in suspended sediment ( $\text{SS-NH}_4^+$ )

Measurements were conducted using the method described by (Maynard et al., 2007). Filters containing suspended solids were placed into polypropylene centrifuge tubes and the  $\text{NH}_4^+$  was then extracted with 10 mL of 2 M KCl for 30 min on an automatic shaking table (160 rpm). Extracts were decanted into additional centrifuge tubes, centrifuged at 4500 rpm for 5 min, and filtered through 0.45  $\mu\text{m}$  inline Whatman® polypropylene Puradisc filters. When immediate analysis was not possible, they were immediately, frozen (-20 °C) until analysis. A second sequential extraction was then performed to extract any residual sediment bound  $\text{NH}_4^+$ . Extracts were analyzed on a Bran and Luebbe Autoanalyzer 3, with a detection limit in extracts of 0.9  $\mu\text{MN}$ , equivalent to 0.09  $\mu\text{MN}$  for a typical sediment mass of 0.1 g. The  $\text{NH}_4^+$  concentrations from the first and second extracts were combined to give a total  $\text{NH}_4^+$  for the suspended sediment samples. Dry weights for sediment samples were obtained by washing residual sediment from filters into centrifuge tubes with MQ water, centrifuging at 4500 rpm for 5 min, then repeating with a further MQ wash and centrifuging stage to remove any residual KCl. Sediments were then oven dried and weighed. This gave concentrations of exchangeable  $\text{NH}_4^+$  of  $\mu\text{g N g}^{-1}$ , which were converted into units of  $\mu\text{MN g}^{-1}$  and then to  $\mu\text{MN}$  by multiplying by the instantaneous suspended sediment concentration (in g L<sup>-1</sup>) at the time of sample collection.  $\text{SS-NH}_4^+$  fluxes ( $\mu\text{MN s}^{-1}$ ) were subsequently

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calculated from the product of the  $\text{NH}_4^+$  concentration and bulk discharge (in L) at the time of sample collection.

## 2.4 Flux calculations

### 2.4.1 Nitrogen fluxes from Leverett Glacier

5 Nitrogen fluxes (June–August) are calculated for LG. LG contributed just under one half of the cumulative glacial runoff to Watson River in summer 2012 (Mikkelsen and Hasholt, 2013; Hawkings et al., 2014). Discharge weighted mean concentrations of dissolved nitrogen species and  $\text{SS-NH}_4^+$  for LG runoff were calculated for the 2012 melt season. Use of discharge weighted mean (DWM) concentrations has the effect  
10 of lowering the mean nitrogen concentrations in bulk meltwaters, since high discharge values are generally accompanied by low nitrogen concentrations. Hence, this method provides a more conservative estimate of nitrogen fluxes. The product of the DWM concentration of each nitrogen species and the runoff flux for June, July and August in 2012 from LG ( $2.2 \text{ km}^3$ ) generated the total seasonal fluxes of these nitrogen species. We  
15 did not measure the particulate organic nitrogen (PON) concentrations in runoff, and in previous years these concentrations have been below the detection limit of standard analytical methods. However, we did calculate the  $\text{SS-NH}_4^+$  fluxes in the same manner as the dissolved nitrogen species. Total fluxes of dissolved and  $\text{SS-NH}_4^+$  in LG runoff during the 2012 melt season are presented in Table 2.

### 2.4.2 Nitrogen fluxes from the Greenland Ice Sheet

20 Currently, there are no other seasonal time series of nitrogen concentrations in runoff from large Greenland outlet glaciers. Hence, nitrogen concentrations in LG runoff are employed in order to generate order of magnitude flux estimates for nitrogen associated with Greenland freshwater export. These are the best possible estimates at the  
25 time of publication. We base our calculations upon the premise that LG is represen-

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indicate that the nitrogen content of ice containing even trace amounts of debris may display nitrogen concentrations which are five times higher than in ice with no debris (Table 1).

### 3 Results and discussion

#### 3.1 Sources of nitrogen in runoff

The LG runoff time series demonstrates that the GrIS provides a continuous supply of nitrogen to downstream ecosystems throughout the main melt period (Fig. 2). Concentrations of TDN are significant (1–10  $\mu\text{M}$ ) and mean nitrate concentrations (1.8  $\mu\text{M}$ ) alone are higher than those often reported in surface ocean and fjord waters ( $< 0.1$ –1  $\mu\text{M}$ ) in western Greenland in summer (Nielsen and Hansen, 1999; Arendt et al., 2010). Higher concentrations of nitrate are observed in deeper ocean waters, but upward diffusion and advection are often limited by a stratified water column during the summer months (Arendt et al., 2010). DIN, which is readily available to marine phytoplankton, accounts for half of the TDN in LG runoff, supplemented by  $\text{SS-NH}_4^+$  from the ice sheet bed. A component of the DIN measured in LG runoff originates from natural and anthropogenic atmospheric sources, via melting of snow and ice (Wolff, 2013) (Table 1). LG drains a large catchment (600  $\text{km}^2$ ) with a high altitudinal range (extending to  $> 1200$  m a.s.l.). New moulins open up and surface lakes drain with snow line retreat (Bartholomew et al., 2011), providing a mechanism by which new sources of DIN are fed to runoff. Water fluxes control the overall nitrogen flux which rises through summer to attain high values during the sampling period in mid-July (Fig. 2). The bulk runoff chemical sampling record did not extend beyond this point. However, we assert that runoff nitrogen fluxes will continue to be high in late July/early August, as evidenced by the sustained high fluxes of nitrogen species in moulin waters up until 9 August (Day 222, Supplement Fig. S5). This is significant given the reported nitrogen limitation of fjord and marine phytoplankton in mid-summer, once the water column becomes more

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stratified and deep marine sources of nitrogen become more inaccessible (Rysgaard et al., 1999; Budeus and Schneider, 1995).

A striking feature of the runoff dataset is the factor of four increase in concentrations of TDN in LG runoff ( $4.5, 5.7 \mu\text{M}$  including  $\text{SS-NH}_4^+$ ) compared with those in snow and ice ( $< 1 \mu\text{M}$ ), reflecting enhancements in dissolved organic nitrogen, ammonium and nitrate (Fig. 3, Table 1). Similar findings have been reported at small valley glaciers (Hodson et al., 2008), and imply the acquisition of significant quantities of nitrogen within the glacier. A substantial proportion of this enhancement must occur in sedimentary environments at the ice sheet bed, as indicated by a significant association between TDN in moulin waters and bulk runoff, but a positive intercept of  $2 \mu\text{M} \pm 0.6$  (Fig. 4). A range of possible sources exist for this additional nitrogen in runoff. For nitrate, enhancement is very likely to occur in the subglacial environment, since nitrate concentrations in moulin waters and snow/ice are similar (Table 1). The basal regions of ice sheets are viable habitats for microbial life and previous work has demonstrated the activity of nitrifying bacteria, which transform ammonium to nitrate (Boyd et al., 2011). In support of this, long-term incubation experiments using LG subglacial sediments (Fig. 5) show the release of up to  $5 \mu\text{M}$  nitrate under aerobic conditions. The simultaneous removal of ammonium ions is consistent with nitrification as the source of this nitrate, likely in more aerobic subglacial channel-marginal sedimentary environments.

The enhancement of ammonium and DON concentrations in moulin waters relative to snow and ice, and in runoff relative to moulin waters is also significant (independent  $t$  test,  $p = 0.05$ ) and suggests the acquisition of these species in surface and basal ecosystems respectively. Likely surface sources are cryoconite holes and debris-rich ice, which display elevated ammonium and DON concentrations relative to pre-melt ice and snow (Fig. 2, Table 1). These debris-laden environments support diverse microbial communities, which actively fix carbon dioxide from the atmosphere (Stibal et al., 2012). We assert that mineralization of organic matter in such environments generates the elevated ammonium concentrations in surface waters (Stibal et al., 2012), while DON is generated by microbial activity or by leaching from allochthonous

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organic matter in debris. The factor of two enhancement in mean ammonium (dissolved + sediment-bound) and DON concentrations in runoff relative to moulin waters suggests an even greater subglacial input of these nitrogen species. Runoff DON and ammonium concentrations are often elevated during subglacial outburst events (Figs. 2 and 6). These events are known to expel long-term stored meltwaters and sediments from beneath the ice sheet (Bartholomew et al., 2011), and the elevated runoff DON and ammonium during such events implies a source in subglacial sedimentary ecosystems. We propose that the subglacial acquisition of DON and ammonium reflects in situ microbial activity, as reported beneath smaller valley glaciers (Hodson et al., 2005). The low dissolved organic carbon (DOC) : DON ratio in runoff (mean = 9.5, DOC data from Hawkings, 2015) is similar to other world glaciers (Hood and Scott, 2008) and is consistent with a microbial source for DON. It contrasts with the higher mean DOC : DON ratios for Arctic rivers (mean = 48) which include a greater terrestrial contribution (Lobbess et al., 2000). These findings support the notion that dissolved organic matter exported from the GrIS may be highly bioavailable to marine bacteria (Lawson et al., 2014, 2013; Bhatia et al., 2010), as has been suggested for glacier systems elsewhere (Hood et al., 2009).

### 3.2 Fluxes of nitrogen from Leverett Glacier

Total dissolved nitrogen (including  $\text{SS-NH}_4^+$ ) fluxes from LG in summer are of the order of 0.10 Gg (Table 2). The estimated TDN yields for the Leverett Glacier catchment arising from this flux are  $164 \text{ kg m}^{-2}$  ( $97 \text{ kg m}^{-2}$  excluding  $\text{SS-NH}_4^+$ ), which is approximately double the typical annual TDN yields measured in large Arctic rivers ( $36\text{--}81 \text{ kg m}^{-2}$ ) (Holmes et al., 2012). This high yield largely arises from the high specific water yield at LG ( $3.7 \times 10^6 \text{ m}^3 \text{ m}^{-2} \text{ a}^{-1}$ ), in comparison to the mean water yield of the largest Arctic rivers, which is two orders of magnitude lower ( $9.3 \times 10^4 \text{ m}^3 \text{ m}^{-2} \text{ a}^{-1}$ ) (Holmes et al., 2012). This implies that there is a much higher continuous flux of dissolved nitrogen species per unit area from the ice sheet than from high Arctic River catchments, which



reflects the acquisition of dissolved N species from both melting snow and ice on the surface and sedimentary environments at the ice sheet bed.

### 3.3 Fluxes of nitrogen from the Greenland Ice Sheet

The estimated summer TN flux from the GrIS is ~ 30 Gg (2000–2011) and 40 Gg (2012) (Table 3). This is a similar order of magnitude to a large Arctic river (the average TDN flux for the Lena, Yenisey, Ob Rivers, July–October is 41 Gg, Holmes et al., 2012). It is notable that the glacial nitrogen fluxes largely supply different ocean basins to the Arctic rivers (Bamber et al., 2012; Holmes et al., 2012). We contend that ice sheet derived nitrogen fluxes are likely to rise with enhanced melting in a warmer climate and could, therefore, stimulate increased primary production in downstream coastal ecosystems. Evidence from a single melt year certainly suggests that within-season fluxes of nitrogen species rise with increasing glacial water flux (Fig. 2). The degree of future nitrogen flux increase in warm melt years, however, is difficult to predict. The atmospheric nitrogen flux (largely as DIN) may scale with increasing melt volumes, but the magnitude of increase will depend upon the availability of glacial ice and snow from post-industrial times, since these display elevated atmospheric DIN compared with pre-industrial ice (Olivier et al., 2006). DON and non-atmospheric ammonium fluxes might also be expected to increase as the zone of melting expands and there is more extensive contact of meltwater with organic matter in surface and subglacial ecosystems. The impact of these present and future nitrogen fluxes upon fjord and coastal marine ecosystems around Greenland is unknown, and requires further study. The input of nutrients associated with Greenland icebergs and runoff may sustain elevated primary productivity beyond the spring phytoplankton bloom, and offers one possible explanation for the reported mid-summer phytoplankton bloom in Western Greenland (Frajka-Williams and Rhines, 2010; Nielsen and Hansen, 1999). It is notable that nitrogen limitation is common in fjord and coastal waters in summer, and hence any increase in DIN supply has the potential to enhance primary productivity.

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## 4 Conclusions

In summary, our findings suggest that the Greenland Ice Sheet provides a continuous source of dissolved nitrogen in runoff through the summer months, a proportion of which is likely to originate from microbial ecosystems on and beneath the ice. The degree to which these GrIS nitrogen fluxes are modified by proglacial processes is unknown, as are the potential impacts upon fjord and coastal marine biological productivity. However, it is well established that phytoplankton in coastal Greenlandic waters often become limited by nitrogen availability by mid-summer, when the glacial nitrogen flux to coastal waters is highest. Fluxes of nitrogen from the ice sheet are similar in magnitude to those of a large Arctic river, and TDN yields are an order of magnitude higher than those reported for Arctic rivers, a reflection of the high surface melt rates (and hence water fluxes) and continuous nitrogen supply from several sources within the ice sheet. Our findings suggest that a melting GrIS may be an important source of nitrogen to downstream ecosystems, and that these nitrogen fluxes may increase in a warming climate.

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**Table 1.** Mean concentrations of nitrogen species reported in LG runoff (including discharge weighted mean, DWM for TDN species), in comparison to those in moulin waters, surface ice (pre-melt and post-melt “Summer ice”, where the latter samples were at the melting temperature and contained dispersed debris), snow, cryoconite water and basal ice.

	NO <sub>3</sub> <sup>-</sup> (μM)			NH <sub>4</sub> <sup>+</sup> (μM)			DIN (μM)			DON (μM)			TDN (μM)		
	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD	n
Bulk runoff-dissolved	1.8	1.2	62	0.4	0.6	62	2.2	1.4	62	2.3	1.5	62	4.5	2.3	62
Bulk runoff-dissolved, DWM	1.1	–	–	0.4	–	–	1.5	–	–	1.7	–	–	3.2	–	–
Bulk runoff-sediment bound	n.d.	n.d.	–	1.2	0.6	39	1.2	n.d.	–	n.d.	n.d.	–	1.2	n.d.	–
Moulins (same period)	0.7	1.4	28	0.6	0.5	28	2.0	1.2	28	1.1	1.3	28	2.2	1.4	28
SURFACE															
Pre-melt ice <sup>a</sup>	0.59	0.14	6	0.3	0.1	6	0.9	0.3	6	0.0	0.0	6	0.6	0.1	6
Snow <sup>a</sup>	1.03	0.17	3	0.45	0.0	3	1.1	0.2	3	0.0	0.0	3	1.02	0.14	3
GrIS ice cores <sup>b</sup>	0.97	n.d.	–	0.45	n.d.	–	1.4	n.d.	–	n.d.	n.d.	–	n.d.	n.d.	–
Summer ice	0.64	0.42	7	0.6	0.6	7	1.3	0.9	7	3.0	2.6	7	2.9	2.1	7
Cryoconite meltwater	1.4	0.4	6	1.1	1.3	6	1.7	0.9	6	0.7	0.4	6	2.4	1.1	6
SUBGLACIAL															
Basal ice	1.5	0.0	6	2.7	0.1	6	3.7	0.1	6	12	1.3	6	15	1.3	6
Incubations (aerobic)	1.4	2.1	7	2.5	2.2	7	3.9	2.5	7	3.36	2	7	7.1	1.7	7
Incubations (anaerobic)	1.03	1.4	6	0.76	0.2	6	1.8	1.3	6	1.79	1	6	5.3	1.4	6

<sup>a</sup> Telling et al. (2012).

<sup>b</sup> Wolff (2013).



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**Table 2.** Estimates of seasonal fluxes of total dissolved (TDN) and particulate nitrogen (SS-NH<sub>4</sub><sup>+</sup>) species (total nitrogen = TN) from Leverett Glacier and the Greenland Ice Sheet in 2000–2010 and 2012.

Glacial Runoff							Icebergs			Total N Fluxes		
GriS Water Flux <sup>a</sup> (km <sup>3</sup> a <sup>-1</sup> ) (2000–2011)	418							~ 600				
GriS Water Flux <sup>a</sup> (km <sup>3</sup> a <sup>-1</sup> ) (2012)	665							~ 600				
LG Water Flux <sup>b</sup> (km <sup>3</sup> a <sup>-1</sup> ) (2012)	2.2							0				
Arctic River mean summer water flux <sup>c</sup> (km <sup>3</sup> a <sup>-1</sup> )	169											
Nitrogen species	TDN	DIN	DON	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	SS-NH <sub>4</sub> <sup>+</sup> -N	TDN	DIN	DON	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	TDN (inc. SS-NH <sub>4</sub> <sup>+</sup> )
Concentration Arctic Rivers <sup>d</sup> (μM)	14	2.7	12	2.0	0.7	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Concentration LG (μM)	3.2	1.5	1.7	1.1	0.4	1.4	1.4	1.4	0.0	1.0	0.5	n/a
Mean summer flux Arctic Rivers <sup>e</sup> (Gg a <sup>-1</sup> )	41	8.8	33	7.7	< 0.5	n.d.	n/a	n/a	n/a	n/a	n/a	41
Flux GriS (Gg a <sup>-1</sup> ): 2000–2010	19	9	10	6	2	8	12	12	0.0	8	4	31
Flux GriS (Gg a <sup>-1</sup> ): 2012	30	14	16	10	4	13	12	12	0.0	8	4	42
Flux LG (Gg a <sup>-1</sup> ): 2012	0.10	0.05	0.05	0.03	0.01	0.04	n/a	n/a	n/a	n/a	n/a	0.10

<sup>a</sup> Tedesco et al. (2012) mean modelled GriS runoff for 2000–2011 and 2012 runoff, Bamberg et al. (2012) for mean ice discharge fluxes.

<sup>b</sup> Measured water flux from Leverett Glacier.

<sup>c</sup> Average summer water flux for 6 major Arctic rivers, Holmes et al. (2012).

<sup>d</sup> Measured concentrations of N species for typical Arctic rivers, Lobbes et al. (2000).

<sup>e</sup> Average summer nitrogen fluxes (July–October) from 6 major Arctic rivers, 1999–2008, Holmes et al. (2012), no data exists for SS-NH<sub>4</sub><sup>+</sup>.

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**Figure 1.** Map showing the study area, including the location of Leverett Glacier runoff sampling station (white dot) and surface sampling site (red dot), together with Søndre Strømfjord and the two other major runoff sources to the fjord (Umivit River and Sarfartoq River).

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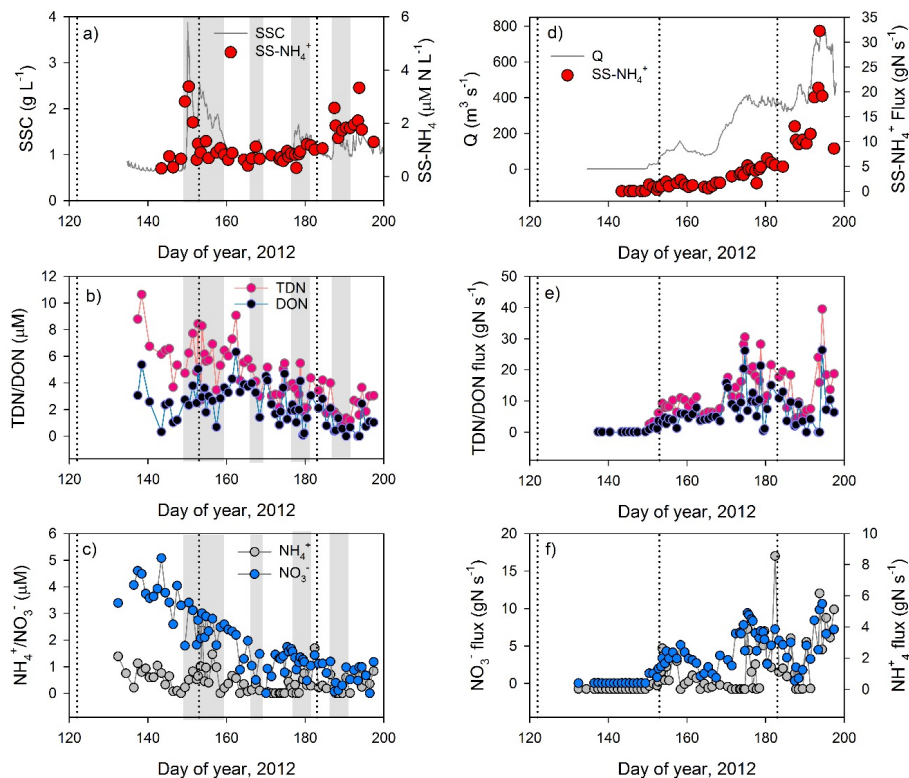
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**Figure 2.** Times series of nitrogen species in LG runoff from the 2012 melt season depicting concentrations of **(a)** bulk meltwater suspended sediment and sediment-bound ammonium ( $\text{SS-NH}_4^+$ ) **(b)** TDN and DON, **(c)** dissolved nitrate and ammonium, and instantaneous fluxes of, **(d)**  $\text{SS-NH}_4^+$  (bulk meltwater discharge,  $Q$ , is also shown), **(e)** TDN and DON and **(f)** dissolved nitrate and ammonium. Vertical dotted lines (left to right) indicate 1 May, 1 June and 1 July 2012.

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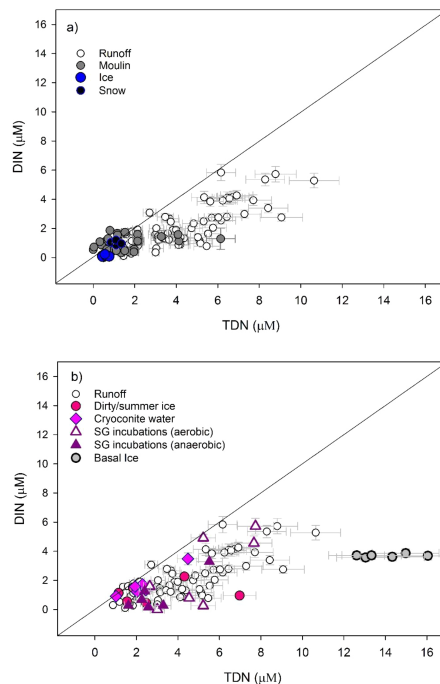
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**Figure 3.** Associations between TDN and DIN in **(a)** runoff, moulin waters, snow and pre-melt ice, where data on snow and pre-melt ice are from (Wolff, 2013; Telling et al., 2012) and **(b)** runoff and glacier surface ecosystems (cryoconite holes, summer ice including dispersed debris) and subglacial ecosystems (basal ice and meltwaters sampled from anaerobic/aerobic long-term subglacial (SG) incubation experiments). A line indicates ratios of 1 for TDN/DIN where the TDN content of samples is entirely comprised of DIN. Samples that plot below this line have a dissolved organic nitrogen component. All samples have been blank corrected and error bars reflect the uncertainty of nutrient analyses given known precision and accuracy.

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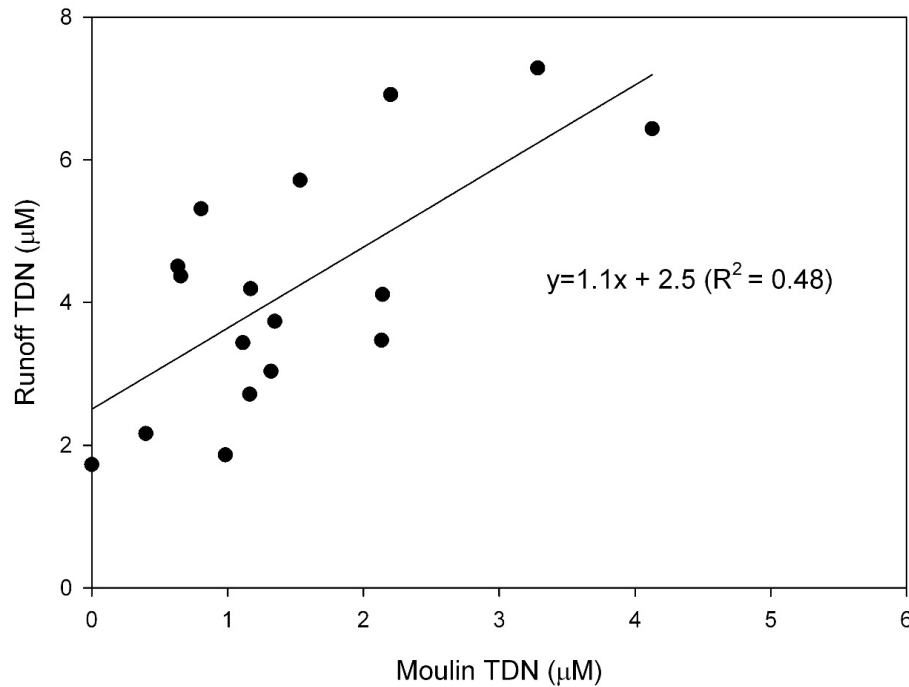
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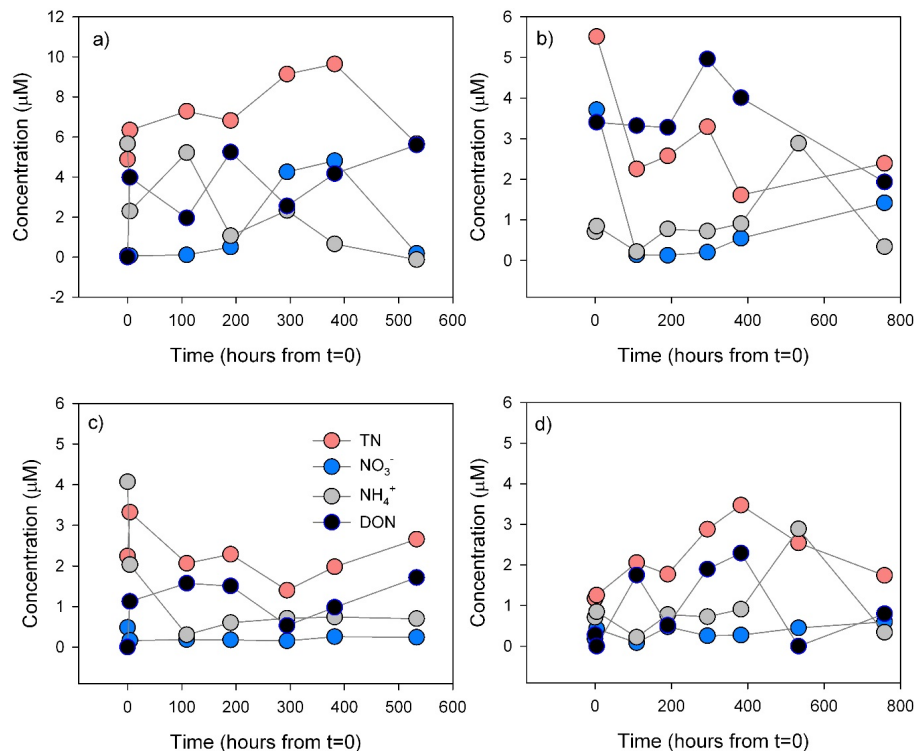
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**Figure 4.** Association between the TDN concentrations measured simultaneously at the moulin and runoff monitoring sites (the correlation is significant at the 99 % confidence level).

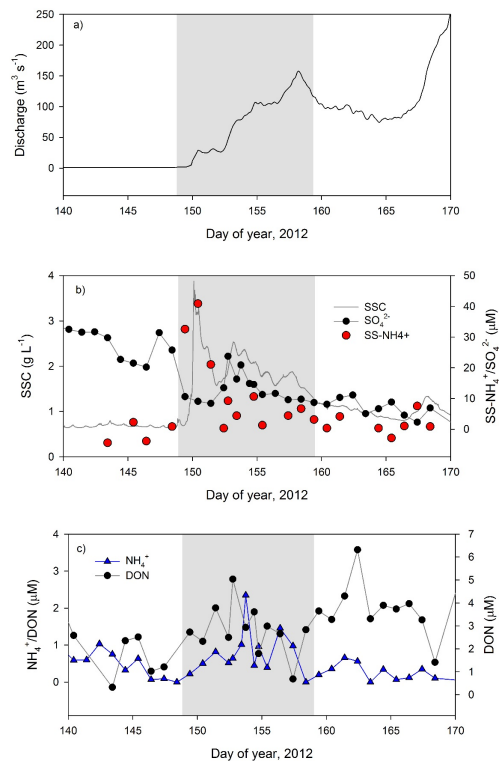
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**Figure 5.** Time series of dissolved nitrogen concentrations measured in **(a)** live aerobic, **(b)** live anaerobic **(c)** sediment-free aerobic and **(d)** sediment-free anaerobic incubation experiments (note the difference in scale for the y axis between **(a)** and **(b–d)**).

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**Figure 6.** Times series of **(a)** bulk discharge, **(b)** concentrations of sediment-bound  $\text{NH}_4^+$  ( $\text{P-NH}_4^+$ ) and dissolved sulphate and **(c)** concentrations of DON and dissolved  $\text{NH}_4^+$  in runoff measured during the first and main subglacial outburst event (shaded) during the 2012 season.